Novel flame retardant thermoset resin blends derived from a free-radically cured vinylbenzylated phenolic novolac and an unsaturated polyester for marine composites

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ABSTRACT

A phenolic novolac resin has been chemically reacted with 4-vinylbenzyl chloride to introduce polymerizable vinyl benzyl groups. The modified novolac spontaneously polymerizes like styrene, is physically and chemically compatible with a typical unsaturated polyester (UP) resin, and can be free-radically cured (crosslinked) alone and in mixtures with UP using styrene as a reactive diluent. The cured vinylbenzylated novolac and co-cured blends of it with UP show superior flame retardance to cured UP alone and have potential applications as matrix resins in glass-reinforced composite laminates especially for marine structures.

Keywords: vinylbenzylated, phenolic novolac, unsaturated polyester, blend, fire performance, thermal stability

1. Introduction

Glass-fibre reinforced composite laminates utilising styrene-cured (free-radically crosslinked) unsaturated polyesters (UPs) as the resin matrix are today widely used in the manufacture of strong, light-weight panels for automobiles, trucks, boat hulls and aircraft interiors [1]. There is currently one major disadvantage to such materials however, especially when used in marine composites, and that is their flammability, which arises from the low thermal stability of the resin matrix and the fact that they decomposes to give a variety of flammable degradation products, such as styrene, aliphatic alcohols, aromatic and aliphatic anhydrides, and other hydrocarbon fragments, leaving very little protective char residue [2]. Hitherto, the problem of flammability in UPs has been addressed through the incorporation of flame-retardant additives [3,4], by building reactive flame-retardant groups into the UP structure [3,5] or by replacing some or all of the styrene cross-linking monomer with a more flame-retardant monomer [3,6,7]. These strategies, however, can have deleterious effects on the physical and mechanical properties of the UP and/or can significantly increase material costs. In order to address this problem, we have been investigating a potentially more cost-effective method of flame retarding UPs by co-curing UP with char-forming, and hence more flame-retardant, resins such as phenolic resoles, furan resins and melamine-formaldehyde resins [8–13]. Surprisingly, the blending of UP with other resins has hitherto been used mainly to improve surface finish or to decrease mould shrinkage rather than to improve flame retardance [14, 15]. Our work has demonstrated that whilst flame-retardance may easily be improved by this "blending" approach, it is important that the added resin is co-cured into the matrix if good flame-retardance is to be accompanied by acceptable physical and mechanical properties. Thus furan resins, which do not co-cure with UP, effectively plasticise the UP [12], and simple resoles, which also do not co-cure, lead to phase separated blends displaying two glass-transition temperatures [9]. Of the commercially available resoles so far studied, we have found only allyl-subsituted resoles to be chemically incorporated into the styrene-cured UP matrix (via radical reactions involving the allyl groups) giving homogeneous blends with single glass transition temperatures (T_gs), good mechanical properties and acceptable flame retardance [9,10]. However, to achieve these properties, the blends have to be subject to a complex curing cycle involving several stages, at temperatures up to 190 ºC in order to fully react free methylol and residual allyl groups, whereas unmodified UPs can be cured at temperatures no higher than 80 ºC. Because of these last observations, we have most recently incorporated into styrene-cured UPs, a phenolic novolac resin (no free methylol groups) chemically modified at the phenolic-OH with methacrylate groups [13]. These groups are incorporated readily into the UP network via copolymerization with styrene and with the unsaturated maleate groups in the backbone of the UP over the normal RT–80 ºC curing cycle for styrene-cured UP resins, giving homogeneous co-cured blends with single T_gs, good

mechanical properties, and acceptable flame retardance. However, the flame retardance of these last blends are not as good (greater total heat release and peak heat release rate) than blends of similar composition based on blends of UP with allyl-functional resoles, probably owing to the ease with which the methacrylate groups depolymerize when heated.

In this paper we describe an alternative modification of novolac, this time with vinylbenzyl groups in an attempt to make a homogeneous, free-radically co-cured phenolic/UP blend with better flame retardance than those made using the methacrylate-functional novolac. The preparation of a flame retardant bearing vinylbenzyl groups was described in 1991 but this was based on a low molecular weight halogenated phenol and not on a phenolic resin [16].

2. Experimental

2.1. Materials

The following materials were obtained from the suppliers indicated and used as received:

Phenolic novolac: Durez 31459 (Sumitomo Bakelite Europe NV), molar mass *ca*. 2500.

4-Vinylbenzyl chloride, 90% (Sigma-Aldrich)

Potassium carbonate, anhydrous, ≥ 99% (Sigma-Aldrich)

p-Benzoquinone (Sigma-Aldrich)

Methyl ethyl ketone (Fisher Scientific)

Diethyl ether (Fisher Scientific)

Unsaturated polyester: Crystic 2.406PA (Scott-Bader), an unsaturated, phthalic anhydride based resin containing *ca*. 35–40 wt% styrene as a reactive solvent, pre-accelerated with 0.2 wt% cobalt octoate.

Catalyst M (Scott-Bader): a free-radical initiator consisting of a solution of MEK peroxide in MEK.

2.2. Synthesis of vinylbenzylated novolac (VB-novolac)

The synthesis of the VB-novolac was carried out according to the reaction scheme shown in Figure 1, i.e. the phenolic groups in the novolac are reacted with 4-vinylbenzyl chloride (VBC) in the presence of weak base to remove the HCl produced by the condensation reaction.

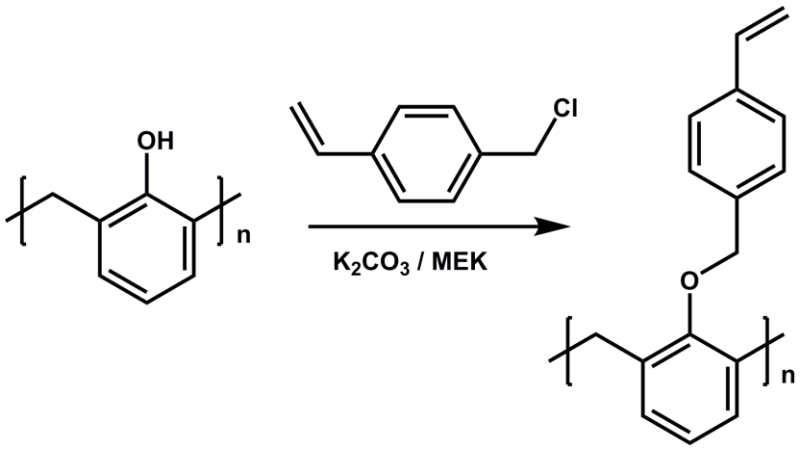

Figure 1. Reaction of phenolic novolac with 4-vinylbenzyl chloride to give VB-novolac.

Novolac (508.8 g, equivalent to 4.8 mol of phenolic rings) was dissolved in 1400 ml of methyl ethyl ketone (MEK) in a 1 L three-neck round bottom flask, purged with nitrogen and equipped with condenser, thermometer and mechanical stirrer. Anhydrous K_2CO_3 (729.3 g, 5.28 mol) was then added to the novolac solution with stirring upon which the solution became orange. To this solution, *p*-benzoquinone (70 ppm) was added (to prevent polymerization of vinylbenzyl chloride), followed by anhydrous sodium iodide (0.8 g, 0.0053 mol). Following this, vinylbenzyl chloride (805.3 g, 5.28 mol) was added slowly, drop-wise at a rate of 1 drop/sec over a period of about 1 h. At the same time, the temperature of the reaction vessel was slowly raised to 80 ^{o}C, at which point another 30 ppm of *p*-benzoquinone was added and heating at 80 ^{o}C continued for another 6 h. Small samples were removed from the reaction vessel at hourly intervals for analysis by size exclusion chromatography (SEC) to monitor the progress of the vinylbenzylation. For the final hour of the 6 h heating period, SEC indicated no significant increase in molar mass of the resin so at the end of this period the reaction mixture was allowed to cool to room temperature.

MEK was then distilled from the reaction vessel by connecting it to distillation column, reducing the pressure to 1000 mbar and heating to 50 ^{o}C. After about 500 ml of the MEK had been removed, 1000 ml of deionised water was added with stirring, followed by 500 ml of diethyl ether. The VB-novolac resin mixture (the organic phase) was then separated from the more dense, yellow aqueous phase using a separation funnel and washed several times with deionised water before a final separation.

The recovered solution of VB-novolac resin in MEK/diethylether was then dried over anhydrous magnesium sulphate and transferred to a round bottom flask fitted with a distillation column, and the MEK/diethyl ether removed by distillation at 30 ^{o}C under a reduced pressure of 1000 mbar. The final

VB-novolac was obtained as a viscous yellow liquid.

Yield: 779.3 g (47.7% of theoretical, assuming complete vinylbenzylation). Number-average molar mass by SEC: 3240. The resin was further characterized by IR spectroscopy to confirm that vinylbenzylation of the novolac had indeed occurred (see Section 3.1).

2.3. Preparation of cured plaques of UP/VB-Novolac blends

Plaques of UP, VB-novolac and UP/VB-Novolac blends were prepared by vigorous hand mixing of UP and VB-Novolac resin in various proportions with the addition of 2 wt% Catalyst M (a free radical initiator), and pouring the resultant mixtures into small circular aluminium moulds of diameter 5.5 cm and depth 3 mm. The method has been described in detail previously [9,13]. These plaques were then allowed to cure at RT for 12 h and then post-cured at various temperatures from 90 ºC to 150 ºC, depending on composition, for periods of up to 12 h, the exact cure procedure being decided on the basis of DSC experiments in which the temperature range over which curing exotherms occurred were monitored (see Section 3.3). In some of the samples, additional styrene was added in various amounts up to that required to approximately match the original styrene content of the UP (*ca*. 30 wt%).

2.4. Characterization of materials

Infrared (IR) spectra of starting materials and products were recorded on a Nicolet iS10 Fourier transform spectrometer equipped with a Smart iTR attachment employing a single bounce diamond crystal.

Molar masses of the parent novolac and of samples of VB-novolac were measured by size exclusion chromatography (SEC) using a VWR/Hitachi Chromaster SEC equipped with a 30 cm column packed with highly crosslinked spolystyrene/divinylbenzene spherical beads having a pore size of 100 Å and capable of resolving molar masses of up to 4000. The instrument was operated at 35 ºC using THF as solvent at a flow rate of 1 ml/min. The columns were calibrated with a set of narrow molar mass polystyrene standards (160–10,000) and thus molar masses of samples quoted in this paper are polystyrene equivalents.

A DSC Q2000 differential scanning calorimeter (DSC) was used to study the curing behaviour of VB-novolac and of UP/VB-novolac blends co-cured using styrene as a crosslinking monomer. Sample size was typically 2–10 mg with a heating rate of 5 ºC/min over the temperature range 30–

350 ºC.

Thermo-oxidative stabilities of cured resins and their blends were assessed by thermogravimetric analysis (TGA) using a TA Instruments SDT 2960 over the temperature range 25–800 ºC using 15 ± 1 mg samples heated at a constant rate of 10 ºC/min in air flowing at 100 ± 5 ml/min.

Dynamic mechanical thermal analysis (DMTA) was carried out on a TA instruments Q800 was used with a single cantilever clamp and multi-frequency set up (0.1 % strain and 1 Hz frequency) over the temperature range 25–350 ºC at 5 ºC/min heating rate. From these experiments, storage moduli were evaluated along with glass transition temperatures (from maxima in plots of tan δ *vs*. *T*)

2.5. Assessment of flame retardance

Limiting oxygen indices (LOI) of cured resins and co-cured resin blends were measured by a standard method (BS 2782) using a Fire Testing Technology (FTT) LOI instrument equipped with an oxygen analyzer.

A cone calorimeter (Fire Testing Technology Ltd. UK) was used to assess the flammability parameters of cured resin systems. Circular samples measuring 5.5 cm in diameter with a nominal thickness of 3 mm were fire tested in the horizontal mode with an ignition source under a radiant heat flux of 50 kW/m^2, similar to that used in our previous work [17]. Before testing, the bottom surfaces and the edges of the samples were wrapped with aluminium foil to ensure that only the top surfaces would be directly exposed to the heat source. A minimum of three tests were performed for each formulation.

3. Results and discussion

3.1. Characterization of VB-novolac

Figure 2 shows IR spectra for the VB-novolac and for the principal reactants: the novolac and vinylbenzyl chloride. It can be seen that the prominent OH stretching band of the phenolic groups in the novolac at around 3400 cm^{-1} is greatly reduced in intensity in the spectrum of VB-novolac, consistent with the phenolic groups in the latter having been significantly vinylbenzylated in the manner shown in Figure 1. Also present in the spectrum of VB-novolac but not in that of the parent novolac are bands at *ca*. 910 and 1000 cm^{-1} characteristic of =CH_2 groups [18]; these bands are

present also in the spectrum of VBC as expected.

The molar masses of the parent novolac and of the VB-novolac were found by SEC to be 2480 and 3240, respectively. If it is assumed that the repeat unit for the novolac and for the vinylbenzylated novolac are as given in Figure 1, i.e the molar masses of the repeat units are 106 and 222 respectively, then full vinylbenzylation would have given a molar mass for the product of 2480/106 × 222 = 5194. Thus the degree of vinylbenzylation for this sample, X, is given by:

$$X \times 5194 + (1\text{-}X) \times 2480 = 3240$$

From this, it can be calculated that X = 0.28, i.e. 28% of the phenolic units have been vinylbenzylated. The number-average molar mass of the unmodified novolac (2480) is consistent with the average chain consisting of 2480/106, i.e. 23.4, methylene phenol repeat units. This figure, combined with a degree of vinylbenzylation of 28%, suggests that on average, 23.4 × 0.28, i.e. 6.5 of the phenolic units in each novolac chain have been vinylbenzylated, with 16.9 per chain remaining unmodified.

Assuming that the amount of resin recovered at the end of the VB-novolac preparation represents quantitative recovery of modified resin; the weight data too (see Section 2.2) can be used to evaluate the degree of vinylbenzylation. Thus, 508.8 g of novolac gave 779.3 g of modified resin and so, degree of vinylbenzylation, X is given by:

$$X \times 1633.8 + (1\text{-}X) \times 508.8 = 779.3$$

Thus, by this method of assessment, X = 0.24, i.e. 24% of the phenolic units have been vinylbenzylated. This value of X is very close to that evaluated from the SEC data, indicating that recovery of the modified resin was close to quantitative and that the degree of vinylbenzylation is around 0.24–028.

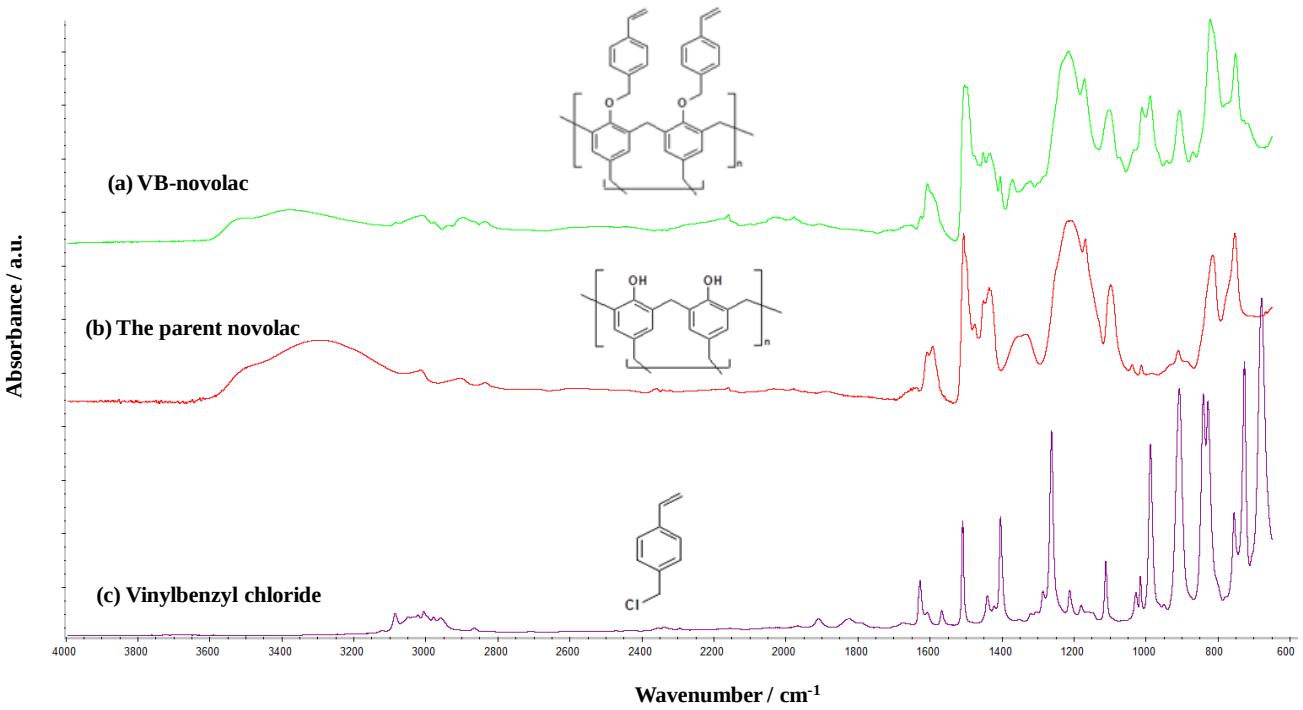

Figure 2. IR spectra of (a) VB-novolac, (b) the parent novolac and (c) vinylbenzyl chloride

3.2. Curing (crosslinking) of VB-novolac

When a sample of VB-novolac was heated in the DSC at 5 ºC/min between 35 and 300 ºC, clear signs of curing were seen in the form of exothermic peaks with maxima at *ca*. 180 and 250 ºC. The DSC of the resin cured at room temperature for 12 h and at 80 ºC for 6 h (similar to that used for curing of UP) showed that both exothermic resin still remained, though shifted to slightly higher temperatures, 210 and 260 ºC respectively, Figure 3(a). The exotherms are thought to arise from a spontaneous polymerization of the vinylbenzyl groups in the VB-novolac, which probably takes place via a free-radical mechanism similar to that for the spontaneous thermal polymerization of styrene [19]. The positions of these exotherms were found to be influenced by the extent to which the sample had been degassed, probably owing to the influence of dissolved oxygen, a known retarder of radical polymerizations, on rates of reaction [20]. In order to cure VB-novolac at temperatures comparable to those used to cure UP, 2 wt% Catalyst M was added. The DSC trace for such a sample is shown in Figure 3(b) in which a sharp exotherm can be seen now at the much lower temperature of *ca* 80 ºC. However, this sample still exhibits a small exotherm at *ca* 250 ºC indicating that polymerization is not complete at 80 ºC. This small exotherm is still present in the DSC trace of a sample of VB-novolac cured external to the DSC machine at RT for 12 h followed by 80 ºC for 6 h, Figure 3(c), again showing the potential for further curing at temperatures well beyond the usual curing temperatures.

Based on these DSC results, final curing conditions of RT for 12 h, 80 ºC for 6 h and then 110 ºC for 3 h with a ramp rate between temperatures of 1 ºC/min were chosen as the optimum, giving an extent of cure of at least 80% based on measurements of DSC exotherm peak areas. Cured VB-novolac is a clear, transparent pale yellow glass.

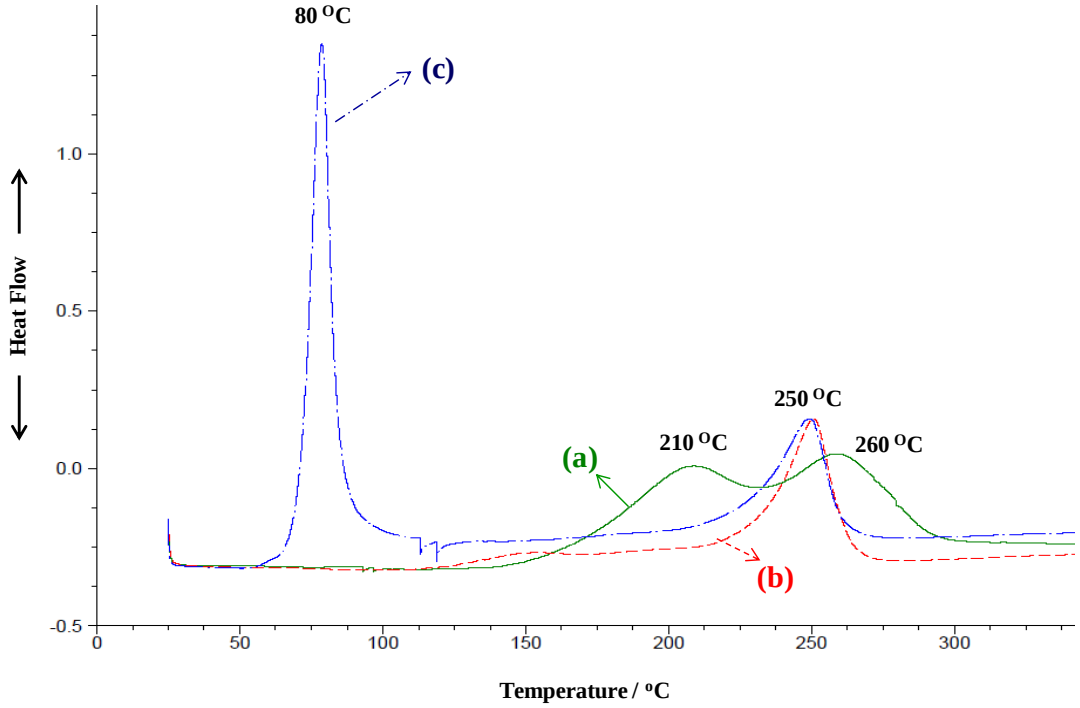

Figure 3. DSC traces of (a) a sample of VB-novolac previously heated at RT for 12 h and 80 ºC for 6 h, (b) a sample of VB-novolac to which 2 wt% Catalyst M has been added and (c) a sample of VB-novolac containing 2 wt% Catalyst M cured at RT for 12 h and 80 ºC for 6 h prior to the DSC experiment.

IR spectra of VB-novolac before and after heating to 300 ºC confirm the polymerization of the vinylbenzyl groups: the characteristic stretching vibrations of the $=CH_2$ groups at *ca*. 1000 cm^{-1} and 910 cm^{-1}, seen in the spectrum of the uncured resin, Figure 4(a), are now absent, Figure 4(b).

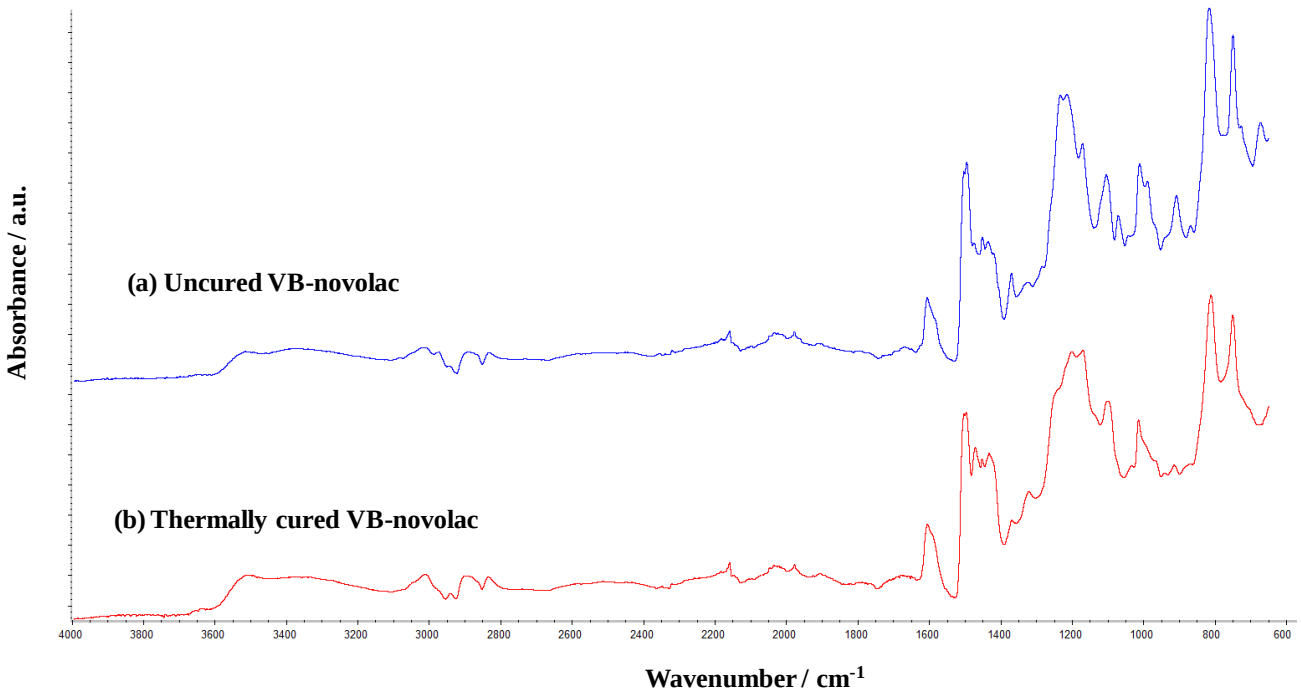

Figure 4. IR spectra of (a) uncured VB-novolac and (b) thermally cured VB-novolac (no added initiator)

3.3. Curing of UP/VB-novolac resin blends

DSC was used to monitor the curing reactions also of UP/VB-novolac resin blends and to establish conditions suitable for ensuring their extensive cure. 70/30 blends of UP with VB-novolac were found to cure readily, but for 50/50 blends, samples appeared more homogeneous after curing if additional styrene was added. Typical amounts used were 10, 15 and 30 wt% based on the VB-novolac content. These amounts of styrene are in addition to that already present in the UP as supplied by Scott-Bader (35–40 wt%). The details of these samples are given in Table 1. The optimum curing conditions for 70/30 UP/VB-novolac blends were established as: RT for 12 h, 80°C for 6 h, and 110°C for 3 h (with an intermediate heating rate of 1 °C/min)**.** For 50/50 blends, curing conditions of RT for 12 h, 90 °C for 8 h (with an intermediate heating rate of 1 °C/min) and finally 110 °C for 3 h (with an intermediate heating rate of 0.3 °C/min), were chosen.

3.4. *Glass transition temperatures and moduli of cured resins and resin blends*

Plots of tan δ *vs T* for various cured resins and resin blends are shown in Figure 5. It can be seen from these plots that single tan δ maxima are seen for all samples except for the sample of VB-novolac cured after the addition of 2% of Catalyst M, which displays two maxima. We conclude that all resin

samples, apart from the VB-novolac, are homogeneous materials, uniformly cured throughout. That the VB-novolac appears inhomogeneous may be an indication that the material fails to cure uniformly owing to the macromolecular nature of the material, i.e. because there is no reactive solvent (styrene) present to dilute the system, many of the pendant vinylbenzyl groups of the VB-novolac remain unreacted, even at the end of the curing cycle. A low, or incomplete, degree of cure may be the reason also why the T_g of the UP/VB-novolac 50/50 blend cured with 10 wt% styrene (in addition to that always present in the UP) is lower than that of the other cured resins. The T_gs (tan δ peak maxima) of the various resins are presented in Table 1. From these data we can note that the T_gs of the resin blends are similar to that of the cured UP (with the exception of the UP/VB-novolac blend cured with only 10 wt% additional styrene).

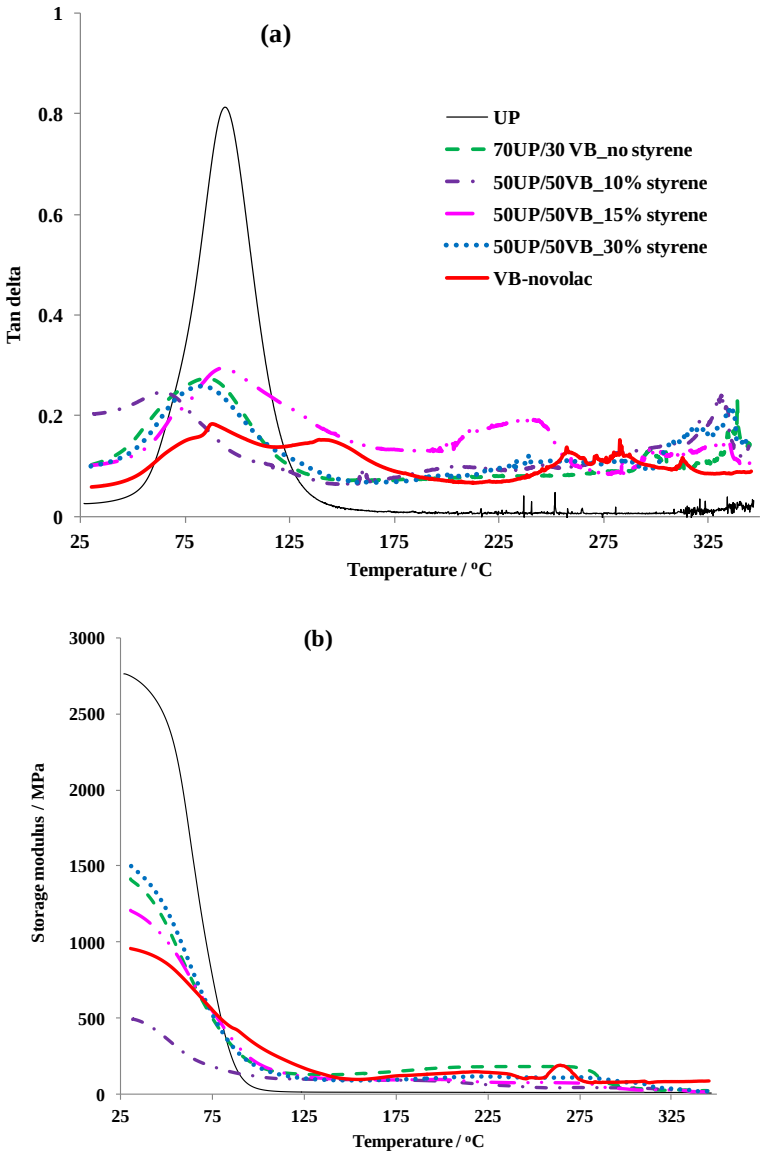

Figure 5. a) Plots of tan δ *vs. T* and b) storage moduli (*E'*) *vs. T* for various cured resins and resin blends

Table 1. Glass transition temperatures (T_g) and storage moduli (E') at 30 ºC for various cured resins and resin blends obtained from Figures 5 (a) and (b), respectively.

Sample	**T_g / ºC**	**E' / MPa**
UP	94	2750
UP/VB-novolac 70/30 (no additional styrene)	85	1411
UP/VB-novolac 50/50 (10 wt% additional styrene)	65	496
UP/VB-novolac 50/50 (15 wt% additional styrene)	93	1210
UP/VB-novolac 50/50 (30 wt% additional styrene)	83	1496
VB-novolac	88, 139	959

Plots of storage modulus (E') *vs.* T for the various cured resins and resin blends obtained from the DMTA experiments are given in Figure 5(b).

Storage moduli at 30 ºC from the data in Figure 5(b) are gathered in Table 1. The moduli for all UP/VB-novolac cured resin blends are lower than that for cured UP, with those for cured VB-novolac and 50/50 UP/VB-novolac cured with only 10 wt% additional styrene most notably so. We take this to be a further indication that these last two resins are incompletely cured, i.e. only loose networks have been formed.

3.5. Thermo-oxidative stabilities of cured resins and resin blends

The thermo-oxidative stabilities of cured resins and resin blends were assessed by TGA runs carried out at a heating rate of 10 ºC/min under air atmosphere. TGA traces for cured UP, cured VB-novolac and cured blends of UP/VB-novolac are shown in Figure 6 with data extracted from these traces given in Table 2.

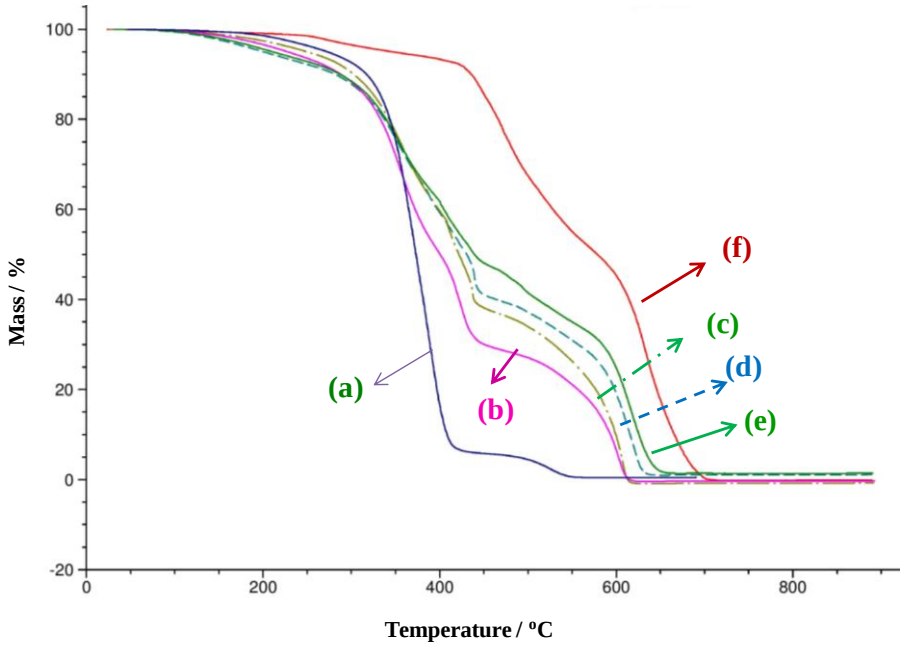

Figure 6. TGA traces recorded at 10 °C/min under air for (a) cured UP, (b) a cured 70/30 UP/VB-novolac blend, (c) a cured 50/50 VB-novolac blend with 15 wt% additional styrene, (d) a cured 50/50 VB-novolac blend with 30 wt% additional styrene, (e) a cured 50/50 VB-novolac blend with no additional styrene, and (f) cured VB-novolac. In all cases, 2 wt% Catalyst M has been added to initiate the free-radical cure reaction.

UP is seen to degrade in two stages, with the first one completing at about 435 °C and representing thermal degradation [10]. Above this temperature oxidation of the decomposition products in the first step occur, leaving no char residue above about 550 °C (represented as $T_{100\%}$ in Table 2) The order of thermo-oxidative stabilities, as judged from the relative positions on the T axis of the mass loss curves are very much as expected, with VB-novolac being the most thermo-oxidatively stable and UP the least. The onset of decomposition temperature, represented by $T_{5\%}$ in Table 2, is 275 °C, while for VB-novolac it is 351 °C. VB-novolac also degrades in two stages, the first one starting after a previous small mass loss at about 430 °C (while in UP by this temperature the first stage has completed) and finishing at about 600 °C. The second stage finishes at 705 °C. The thermo-oxidative stabilities of the blends are intermediate between those of the pure resins, as expected, with the 50/50 UP/VB-novolac blends performing better than the 70/30, again as expected. The styrene content in the 50/50 blends also affects thermo-oxidative performance, with the blend containing 30 wt% additional styrene being less thermo-oxidatively stable than that containing 15 wt% additional styrene, which in turn performs less well than that to which no extra styrene has been added (see

particularly relative amounts of residue remaining at 500 °C and temperatures for 100% mass loss in Table 3). The styrene content also has an effect on the onset temperature for degradation as judged from the $T_{5\%}$ values (see Table 3) and of particular note here is the fact that $T_{5\%}$ is lower for the 50/50 blends containing no additional styrene and 15 wt% additional styrene than for that containing 30 wt% additional styrene. This may a further indication that the 50/50 blends require ca. 30 wt% styrene at least to form a complete, thermally stable crosslinked network as previously suggested on the basis of unexpectedly low T_g values and storage moduli (Section 3.4).

Table 2 also lists the residual mass of all resins at 550 ^oC, chosen as the temperature where the char oxidation of UP is complete, leaving virtually no char residue (0.6%). The high char yield (residual mass at 550 ^oC) for VB-novolac indicates its crosslinking and charring tendency, and hence indicating lower flammability. Table 2 also lists calculated average residual masses at 550 °C, calculated from the residual masses of the pure components at this temperature. For example, for a 50/50 UP/VB-novolac blend, the mass average residual mass at 550 °C is calculated as 50% of residual mass of UP at 600 °C plus 50% of residual mass of VB-novolac at 600 °C. For samples containing extra styrene, the concentration of styrene has been compensated for in the calculations. In all cases the experimental values are higher than the expected averages, indicating some interaction between the two resins. The difference between the experimental and calculated values (Δ residue) however increases with increasing phenolic content in the blend, while with added styrene, the difference decreases (Table 2)

Table 2. TGA analysis data for cured UP, VB-novolac and various UP/VB-novolac blends

Sample	**Temp at mass loss / ºC**		**Residue remaining at 550 ºC / wt%**		
	$T_{5\%}$	$T_{100\%}$	**Experimental**	**Calculated**	**Δ residue (Experimental –Calculated)**
UP	275	550	0.6	–	–
UP/VB-novolac 70/30	227	625	21.2	16.9[a]	4.3
UP/VB-novolac 50/50 with no additional styrene	211	650	35.0	27.8[a*]	7.2
UP/VB-novolac 50/50 with 15 wt% additional styrene	200	636	31.0	25.7[b]	5.3

UP/VB-novolac 50/50 with 30 wt% additional styrene	248	622	26.4	20.5[c]	3.8
VB-novolac	351	705	55.0	–	–

[a,a*] Calculated assuming that char yield in blends are mass averages of those of component resins

[b,c] 92.5 and 85% value of [a*] to compensate for extra styrene

3.6. Limiting oxygen indices (LOI)

LOI values were recorded on plaques of cured UP, VB-novolac and various UP/VB-novolac blends. The higher LOI value of VB-novolac (23.6 vol%) compared with that of UP (18.0 vol%) shows the lower flammability of the former. This value is also higher than that for an allyl-functional phenolic resole (22.2 vol% [10]) and a methacrylate-functional novolac (21.3 vol% [13]) reported in our previous publications.

The LOI of UP/VB-novolac blends are given in Table 3, and indicate a decrease in flammability as the VB-novolac content of a UP/VB-novolac blend is increased. However, the amount of additional styrene in the case of the 50/50 UP/VB-novolac blend appears to make little difference to LOI within the experimental limits of the method. This is more clear from the calculated average values given in Table 3, where 70UP/30VB-novolac has the expected LOI value. For the 50/50 blend without styrene (which could not be prepared) the expected value is 20.8 vol%. With additional styrene the LOI values are higher than expected.

Table 3. LOI values of cured resins and resin blends

Sample	**LOI / vol% O_2**	**Calculated LOI of blends / vol% O_2**
UP	18.0	–
70UP/30VB-novolac (no additional styrene)	19.7	19.7
50UP/50VB-novolac (10 wt% additional styrene)	19.9	18.7
50UP/50VB-novolac (15 wt% additional styrene)	19.8	19.2
50UP/50VB-novolac (30 wt% additional styrene)	20.0	17.7
VB-novolac (no styrene)	23.6	–

Note: The calculated average LOIs of 50/50 blends containing 10, 15 and 31% styrene are 90, 92.5 and 85% of the calculated value of the blend with no styrene (20.8 vol%)

3.7. Cone calorimetry

Cone calorimetry was carried out under a radiant heat flux of 50 kW/m^2 on cured plaques (5.5 cm diameter × 3 mm depth) of the UP, VB-novolac resins and their blends. Plots of heat release rate (HRR) and mass loss *vs*. time (*t*) for the cured resins and resin blends are given in Figures 7 (a) and (b), respectively and all derived cone calorimetric data are presented in Table 4. It can be seen from Figure 7 (a) that both the peak heat release rate (PHRR, peak of the HRR *vs*. *t* curve) and total heat released (THR, area under the curve) are less for the VB-novolac than those for UP, but that time to ignition (TTI) is shorter. The cured 70/30 blend shows behaviour in these respects intermediate between those of the pure components. In 50/50 blends however, the effect of styrene can be clearly seen, i.e., TTI is reduced and the PHRR is increased with increasing styrene content. Smoke production is significantly less for VB-novolac than for UP, with the blends again showing behaviours intermediate between those of the component resins and those with styrene having higher smoke production (Table 4). The mass *vs*. *t* curves also indicate the earlier mass loss of the blends containing styrene. The char formation in VB-novolac and UP/VB-novolac blends is significant, whereas UP alone produces very little char, Figure 7 (b), which can also be seen visually from digital images of the residues in Figure 8. The 50UP/50VB-novolac with 15% styrene shows fragmented char compared to other samples where the char is very compact, indicating that this sample is not completely cross-linked.

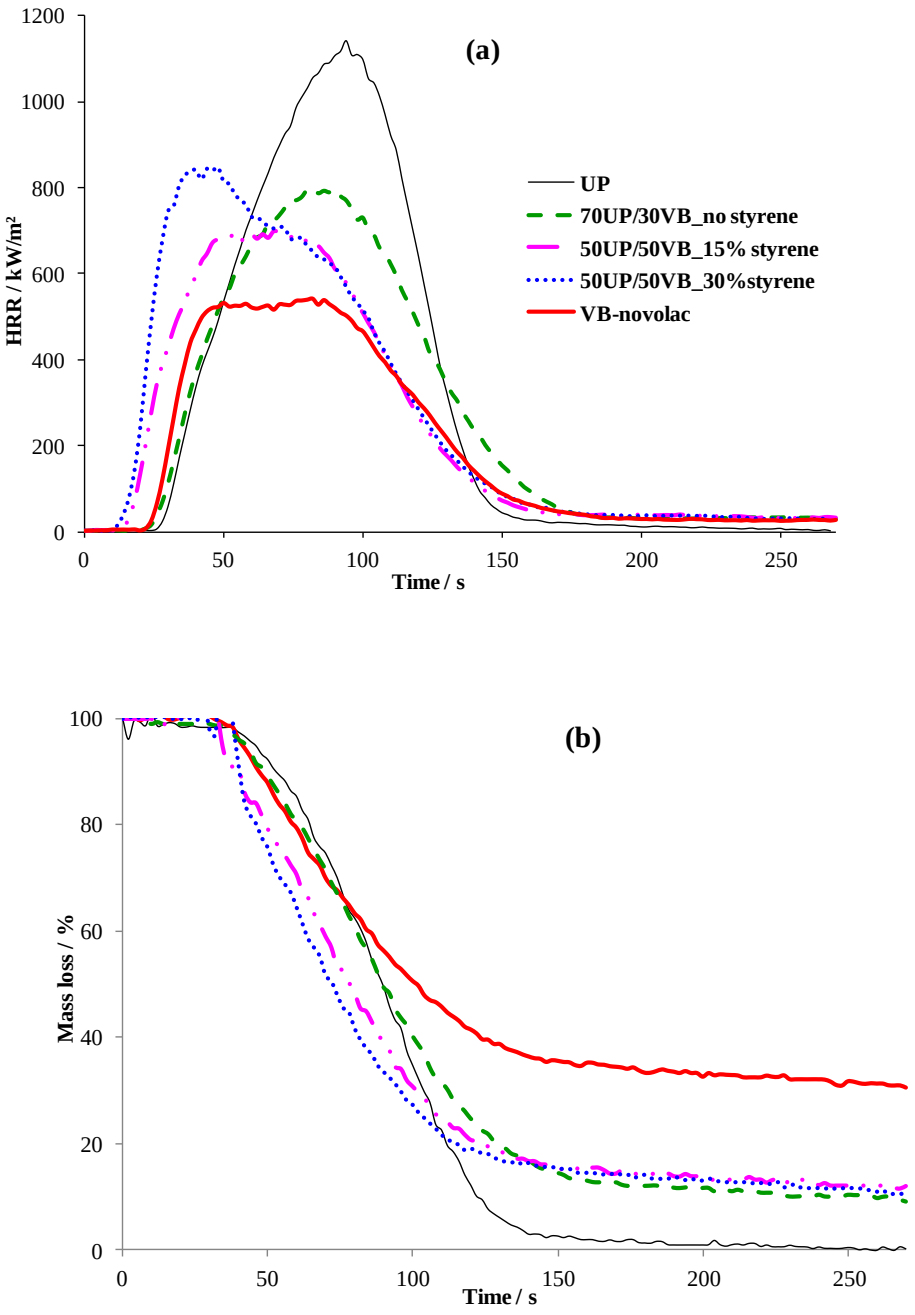

Figure 7. (a) HRR (b), mass loss and c) RSR versus time curves for UP, VB-novolac and their blends obtained by cone calorimetry at 50 kW/m^2 heat flux.

UP | **70UP/30VB_ no styrene** | **50UP/50VB_ 15% styrene** | **50UP/50VB_ 30% styrene** | **VB-novolac**

Figure 8. Digital images of the residues left after the cone experiments of UP, VB-novolac and their blends.

Table 4. Cone calorimetric data acquired from cured resins and UP/VB-novolac resin blends under a radiant heat flux of 50 kW/m

Sample	**TTI / s**	**FO / s**	**PHRR / kW/m²**	**THR / MJ/m²**	**TSR / m²/m²**	**CY / wt%**
UP	34 ± 0	144 ±1	1143 ± 15	80 ± 1	3868 ± 89	1.0
70/30 UP/VB-novolac (no additional styrene)	32 ± 4	174 ± 2	800 ± 19	70 ± 0	3672 ± 50	11.6
50/50 UP/VB-novolac (15 wt% additional styrene)	20 ± 1	154 ± 6	720 ± 80	65 ± 5	3348 ± 210	12.6
50/50 UP/VB-novolac (30 wt% additional styrene)	24 ± 6	152 ± 19	895 ± 113	67 ± 9	3624 ± 309	13.3
VB-novolac (no added styrene)	29 ± 1	160 ± 8	611 ± 43	52 ± 3	2888 ± 78	32.5

Note: TTI = time to ignition; FO = time to flame out; PHRR = peak heat release rate; THR = total heat released; TSR = total smoke released; CY = char yield

In order to compare the flammabilities of VB-novolac and UP/VB-novolac blends with those reported previously of the allyl functional phenolic resole (Allyl-resole) [10] and the methacrylate functional novolac (Methacrylate-novolac) [13] resins and their blends with UP, the changes in LOI and selected cone parameters compared to the UP (Δ parameter = parameter of sample – parameter of UP) are reported in Table 5. In each sample the data used for the UP are taken from the respective data reported with that series of samples (for VB-novolac in Table 4 and for Allyl-resole and Methacrylate-novolac taken from references [10, 13] as also reported in footnote of Table 5). The slight differences in cone results for different UP samples, are apart from the usual ±10% variation,

also due to different batches of the resin used to prepare samples at different times. Some parameters (PHRR, THR, TSR) are also presented as percentage change with respect to the respective parameter of the UP.

It can be seen from these comparative data that cured VB-novolac is signficantly more flame retardant than cured Allyl-resole and cured Methacrylate-novolac i.e., bigger reduction in PHRR and THR (similar to Allyl-resole), and increase in CY and LOI, although it must be noted that cured Methacrylate-novolac was crosslinked with 32 wt% added styrene, a relatively flammable component. The TTI, however, is lower for VB-novolac compared to that of the Allyl-resole. The 70/30 blend of UP with VB-novolac also performs better than the corresponding blends of UP with Allyl-resole and Methacrylate-novolac. For the 50/50 UP/VB-novolac blends, the amount of styrene added has a small effect on flame retardance, with that containing less added styrene (15 wt% against 30 wt%) producing a greater reduction in PHRR and THR as might be expected, given the flammability of styrene. The smoke reduction in VB-novolac and blends however is less than those in Allyl-resole and Methacrylate- novolac resins and their blends.

The mechanism of flame retardance in these blends is predominantly a condensed phase one in which the flammable UP is diluted by a less flammable, char-forming, phenolic-based resin. The incorporation of functional groups in the phenolic component capable of readily undergoing free-radical copolymerization with the crosslinking monomer, styrene, and the maleate unsaturation in the UP chains, enables the phenolic component to form a continuous crosslinked matrix with the UP.

Table 5. Δ parameter (sample – control, UP) for UP/VB-novolac, UP/Allyl resole (derived from data presented in [10]) and UP/Methacrylate-novolac (derived from data presented in [13]) resins blends and pure resins.

Sample	**Δ LOI / vol% O_2**	**Cone calorimetric results**				
		Δ TTI / s	**Δ PHRR / kW/m², (%)**	**Δ THR / MJ/m², (%)**	**Δ TSR / m²/m² (%)**	**Δ CY / wt%**
70UP/30VB-novolac (no additional styrene)	+1.7	-2	-343 *(-30)*	-10.0 *(-13)*	-196 *(-5)*	+10.6
70UP/30Allyl resole [10]	+1.1	+14	-98 *(-9)*	-7.9 *(-10)*	-271 *(-7)*	+10.0
70UP/30Methacrylate-novolac (32 wt% additional styrene) [13]	+1.2	+1	-198 *(-17)*	-15.0 *(-18)*	-904 *(-19)*	+5.7
50UP/50VB-novolac (15 wt% additional styrene)	+1.8	-14	-423 *(-37)*	-15.0 *(-19)*	-520 *(-13)*	+11.6
50UP/50VB-novolac (30 wt% additional styrene)	+2.0	-10	-248 *(-22)*	-13.0 *(-16)*	-244 *(-6)*	+12.3
50UP/50Allyl-resole (no additional styrene) [10]	+1.7	+17	-225 *(-21)*	-17.9 *(-23)*	-924 *(-23)*	+13.0
50UP/50Methacrylate-novolac (32 wt% additional styrene) [13]	+1.8	+1	-290 *(-26)*	-19.0 *(-23)*	-1190 *(-25)*	+10.5
VB-novolac (no styrene)	+5.6	-5	-532 *(-47)*	-28.0 *(-35)*	-980 *(-25)*	+31.5
Allyl-resole (no styrene) [10]	+4.3	+32	-249 *(-24)*	-30.9 *(-39)*	-1881 *(-46)*	+26.0
Methacrylate-novolac (32% additional styrene) [13]	+3.4	+3	-329 *(-29)*	-22.0 *(-27)*	-1301 *(-27)*	+17.8

Notes:

1. Various parameters for the UP in reference [10] are as: LOI =17.9 vol% , TTI = 40s, PHRR = 1053 kW/m^2, THR = 78.9 MJ/m^2, TSR = 4090 m^2/m^2 , CY = 1.0%. In reference [13]: LOI =17.9 vol% , TTI = 38s, PHRR = 1130 kW/m^2, THR = 83.0 MJ/m^2, TSR = 4813 m^2/m^2 , CY = 1.9%.

2. The data in brackets and italic fonts represent the percentage change w.r.t the control sample

3. The (–) and (+) signs represent reductions and enhancements, respectively.

4. Conclusions

A phenolic novolac has been successfully functionalized with vinylbenzyl groups (giving VB-novolac) to the extent of about 45% of the theoretical maximum. This resin spontaneously polymerizes when heated, like styrene, and can also be free-radically co-cured with UP using styrene as a crosslinking monomer. Co-cured blends of UP with VB-novolac are significantly more flame retardant than cured UP itself and than the co-cured blends of UP with an allyl-functional resole

previously studied. A 70/30 blend of UP/VB-novolac also outperforms a blend of UP with a methacrylate-functional novolac of similar composition. Co-cured blends of UP with both VB-novolac and Methacrylate-novolac show significant promise as replacements for cured UP as matrices for more flame-retardant glass reinforced composite laminates. Studies of the properties (flame retardant and mechanical) of laminates based on these new resin blends will be reported elsewhere.

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